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Formation of OH Radicals in the Gas-Phase Reaction of Propene, Isobutene, and Isoprene with O_3: Yields and Mechanistic Implications

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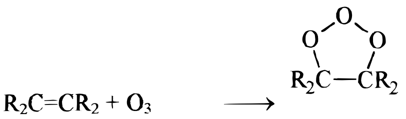
OH radicals originating from the alkene−ozone reaction have been proposed as a relevant source of OH radicals in the lower troposphere. Since the reported yields of OH radicals differ considerably, we redetermined the OH radical yield for three terminal alkenes by performing a series of pseudo-first-order experiments. Ozonolysis studies were carried out under excess ozone conditions in the presence of different cyclohexane concentrations. The decay rate of the alkene (k_{obs}) was followed by long-path FTIR spectroscopy. From the decrease of the effective rate constant ($k_{obs} = k_{eff}[O_3]$) upon addition of cyclohexane, the OH radical yield was determined. The OH radical yields were found to be independent of the concentration of reactants for the Criegee intermediates, which are formed in ozonolysis systems. From these results we conclude that OH radicals are formed in a unimolecular process, presumably from the decomposition of the excited Criegee intermediate. Determined yields of OH radical formation in the ozonolysis of propene, isobutene, and isoprene were 0.34, 0.60, and 0.26, respectively. Detailed product studies were performed to verify if the observed stable products can be explained by the assumption that OH radicals are formed via the hydroperoxide channel as proposed by Niki et al. [*J. Phys. Chem.* **1987**, *91*, 941−946]. For the isobutene−ozone system, experimental product yields were found to agree well with predictions from a chemical mechanism based on the chemistry of the acetonylperoxy radical $CH_3C(O)CH_2O_2$, which is formed as an important radical product from the decomposition of the $(CH_3)_2COO$ Criegee intermediate.

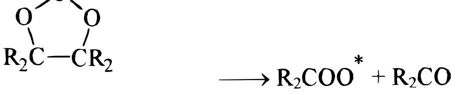
Introduction

The gas-phase reaction of ozone with alkenes is one of the very few reactions of atmospheric interest that are initiated without free radicals. This tropospheric oxidation pathway for unsaturated compounds has received considerable attention because of the reported formation of OH radicals.[1−6] According to a study of Paulson and Orlando,[7] the reaction of ozone with simple anthroprogenic alkenes can produce significant amounts of OH radicals in urban and rural atmospheres. Another aspect of this pathway for OH radical formation is that it is independent of sunlight and therefore might represent a source of OH radicals at night[8] or in indoor environments.[9]

Although the mechanism of the gas-phase ozonolysis is not completely clear and the Criegee intermediate remains to be detected in the gas phase, the formation of the Criegee intermediate (reaction 2) can be explained by the decomposition of the primary ozonide (or molozonide), which represents the primary (unstable) product of the alkene ozonolysis:



(1)



(2)

Mainly on the basis of the studies of Niki et al.[1] and Martinez and Herron,[10] it is widely accepted that the Criegee intermediate can undergo three different decomposition−isomerization pathways in the gas phase, with the star indicating excess vibrational energy:

ester channel

$$R_1CH_2(R_2)COO^* \rightarrow R_1CH_2C(O)OR_2^*$$

$$R_1CH_2C(O)OR_2^* \rightarrow R_1CH_2 + R_2 + CO_2 \qquad (3a)$$

$$R_1CH_2C(O)OR_2^* \rightarrow R_1CH_2R_2 + CO_2 \qquad (3b)$$

hydroperoxide channel

$$R_1CH_2(R_2)COO^* \rightarrow R_1CH{=}C(OOH)R_2^*$$

$$R_1CH{=}C(OOH)R_2^* \rightarrow R_1CH{=}C(O)R_2 + OH \qquad (4)$$

stabilization channel

$$R_1CH_2(R_2)COO^* + M \rightarrow R_1CH_2(R_2)COO + M \qquad (5)$$

An additional decomposition channel for the energy-rich Criegee intermediate, the elimination of $O(^3P)$ atoms, has been observed in the reaction of O_3 with *trans*-1,2-dichloroethene.[11] This potential channel has not been included in the above scheme, since to date little firm evidence for its occurrence in the reactions of O_3 with simple alkenes has been found. So far only upper limits for this channel have been established; all were well below 5%.[12,13]

The mechanism of OH radical formation via the hydroperoxide channel (reaction 4) is supported by the results of Atkinson et al.,[2] who found a quantitative relationship between the extent

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of OH radical formation and the number of H atoms in β-position to the double bond. While the formation of OH radicals via the intermediary formation of a hydroperoxide is the most widely accepted mechanism, Paulson et al.[14] suggested that OH radicals are formed in the reaction of the stabilized Criegee intermediate (formed in reaction 5) with water vapor:

$$R_1CH_2(R_2)COO + H_2O \rightarrow R_1CH_2C(O)R_2 + 2OH \quad (5)$$

In a recent study from this group Schäfer et al.[5] found no evidence for the direct formation of OH radicals in the ozonolysis and proposed that the Criegee intermediate might act as an oxidant for the alkenes and alkanes (if added) present in the chemical system.

So far, most of the reported OH yields are based on either product studies[1,15] or experiments that used added compounds as OH scavenger. The formation of specific products from the oxidation of the OH radical scavengers was used to determine the OH yields by a number of groups.[2,3,16,17] Alternatively, the OH radical yield has been inferred from the decrease in the concentration of the OH radical scavenger.[5,18,19−21] Most of these studies, which were focused on the determination of OH radical yields, do not embed this information in the overall mechanism of the gas-phase ozonolysis. This, however, is crucial, since reported OH yields can be as high as 70−90% for simple alkenes, making the proposed hydroperoxide channel the dominant decomposition channel of the Criegee intermediate. In most of the product studies on the other hand, the observed products are normally attributed directly to one specific decomposition channel of the Criegee intermediate.[13] Consequently, there is some disagreement between the OH radical yields derived in scavenging experiments and OH radical yields determined from product studies, which are typically lower by a factor of 2. On the basis of a product study, Horie and Moortgat[22] derived an OH radical yield of 10% for propene and 17% for *trans*-2-butene, whereas Atkinson and Aschmann[3] determined yields of 33% and 64% for propene and *trans*-2-butene, respectively.

The aim of this study was to introduce an alternative method for the determination of OH radical yields and to combine this information with the results of a product study. OH radical yields are determined by a series of pseudo-first-order experiments in the presence of different amounts of cyclohexane. Under these experimental conditions, OH radicals are expected to react with either the alkene used or with the cyclohexane, if present, and hence, the experimentally determined rate constant for the reaction of the alkene with ozone is dependent on the OH radical yield and the amount of cyclohexane present.

Determined OH radical yields were used as key input parameters for the development of an explicit model, opposite to previous studies,[22] where OH radical yields were inferred from chemical modeling of a complex mechanism. The influence of the peroxy radical chemistry on product distributions was investigated with experiments performed using higher initial concentrations of the reactants. To enable differentiation between products arising from the reaction of O_3 or OH radicals with the alkene, experiments were duplicated in the presence of CO as OH radical scavenger. Isobutene was chosen as the alkene, because much of the chemistry of the $CH_3C(O)CH_2$ radical, which is formed in the hydroperoxide channel of the $(CH_3)_2COO^*$ intermediate (reaction 4), is known from studies investigating the oxidation of acetone.[23,24] An explicit chemical mechanism was set up using the OH radical yield determined in this study and peroxy radical chemistry according to the IUPAC recommendations.[25] It was found that simulated product yields do agree well with experimental data for all measured products except methylglyoxal, which was underestimated by a factor of 2. As a result, it appears that product yields in the isobutene−ozone system strongly depend on the reactions of the peroxy radicals formed. Under conditions of high NO only the formation of CO, CO_2, HCHO, HCOOH, and $CH_3C(O)CH_3$ are expected as stable products from the ozonolysis of isobutene.

Experimental Section

Experiments were carried out in an evacuable, 570 L spherical glass reactor in 730 ± 5 Torr (1 Torr = 133.3224 Pa) of synthetic air. The reaction temperature was kept constant at 296 ± 2 K by the laboratory air conditioner. Details of the design of the reactor have been given elsewhere,[26,27] and only a brief description will be given here.

For the determination of the OH radical yields in the ozonolysis of propene, isobutene, and isoprene, initial concentrations of 1.2×10^{13} molecule cm^{-3} for the alkenes were used, as determined by standard volumetric methods. To maintain pseudo-first-order conditions, the initial concentration of ozone was 1.2×10^{14} molecule cm^{-3}. The IR absorption coefficient of ozone at 1034 cm^{-1} was determined by comparison with the known UV absorption at 253 nm.[28] The alkenes investigated in this study and cyclohexane were calibrated using standard volumetric methods.

After the reactor was filled to about 670 Torr with synthetic air, ozone was produced by the photolysis of oxygen at 193 nm using a Penray UV lamp mounted inside the reactor. After ozone was produced with an approximate concentration of 1.2×10^{14} molecule cm^{-3}, cyclohexane (c-C_6H_{12}) was added as an OH scavenger. The amount of cyclohexane was varied in the experiments, with maximum concentrations of $(9.6-33.6) \times 10^{14}$ molecule cm^{-3} for the different alkenes, which was calculated to scavenge more than 95% of the OH radicals formed during the ozonolysis. Prior to the addition of the alkene, FTIR spectra were recorded to determine the exact amount of ozone, and c-C_6H_{12}, in the reaction chamber.

The decrease of the alkene concentration was monitored by FTIR spectroscopy using an MCT detector at a spectral resolution of 0.5 cm^{-1}. A total of 64 individual scans were coadded for each spectrum, resulting in a temporal resolution of 65 s. To evaluate the absorption−time profiles, only the first five data points, corresponding to an alkene consumption of 35−54%, were used for the linear regression.

Product studies of the isobutene−ozone system were performed in a similar manner with initial concentrations of 4.8×10^{14} and 2.4×10^{14} molecule cm^{-3} for isobutene and ozone, respectively. In these experiments, 256 scans were coadded for each FTIR spectrum. To scavenge OH radicals formed in the gas-phase ozonolysis, experiments also were carried out in the presence of 5% CO, which is well below the lower explosive limit for CO (12.4%). Products were quantified by comparing the absorbance with spectra of calibrated reference compounds. Since the statistical error of the calibration is not sufficient to account for the overall uncertainties in the determination of the products, errors were estimated as follows: isobutene, ozone 5%; HCHO, HCOOH, acetone, CO 10%; methylglyoxal, hydroxyacetone, CO_2, ketene, CH_3OH 20%. Chemicals were used as purchased commercially: propene (Messer Griesheim), isobutene, isoprene, and cyclohexane from Aldrich.

For part of this study an attempt is made to verify experimental product yields with numerical simulations using the FACSIMILE computer program.[29] Owing to the uncertainties associated with complex chemical mechanisms, the influence of the error of the rate constants and the branching ratios for the various chemical reactions was carefully investigated. The chemical scheme used in the simulation is shown in Table 4. If available, rate constants and associated errors were taken from the IUPAC recommendation.[25] To ensure symmetrical errors, these are given in the IUPAC recommendation as $E = \Delta \log(k)$. If $\Delta \log(k)$ is thus given as 0.15, the corresponding rate constant k has lower and higher limits of $k \times 10^{(1-0.15)}$ and $k \times 10^{(1+0.15)}$, respectively. For the present study it was assumed that the given error $\log(\Delta k)$ is normally distributed around $\log k$ with $\log(\Delta k)$ representing two standard deviations. Rate constants that are not available from the IUPAC recommendations were calculated using the geometric mean rule.[13] In this case errors for estimated rate constants were taken as $\Delta \log(k) = 1.0$ corresponding to an uncertainty of a factor of 10. Branching ratios were varied linearly within the given limits (see Table 4), since the assumption of normal distributed branching ratios may yield negative branching ratios.

To obtain a measure of the overall uncertainties of the chemical mechanism shown in Table 4, a "Monte Carlo" type approach with a total of 3000 simulations for each experiment was performed. Simulations using the FACSIMILE computer program are based on an ASCII input file containing all relevant information such as rate constants, reactions, and output instructions. To test the effect of changed rate constants, this input file was processed by a simple self-written computer program that changes the rate constants in their specified error limits. The manipulated file serves as the input file for the FACSIMILE simulation. At the time experimental yields were determined, the simulation was stopped and calculated concentrations were stored. The procedure was repeated in a loop until the desired number of simulations ($n = 3000$) was reached.

Results

Determination of OH Radical Yield. For the determination of OH radical yields, a series of experiments (no. of experiments = 8−15) was performed for each of the alkenes. Experimental conditions were chosen so that the monitored decay of the alkene absorption follows pseudo-first-order kinetics. By use of an initial O_3 concentration of 1.2×10^{14} molecule cm^{-3} (corresponding to a 10-fold excess over the alkene), the absorption of the alkene was monitored by long-path FTIR spectroscopy. In Figure 1 absorption profiles are shown for the reaction of isobutene with ozone in the presence of different amounts of c-C_6H_{12}. The decrease in alkene absorption could be described in all cases by a linear function in a semilog plot, although some deviation from purely linear behavior was observed. This nonlinear behavior was more pronounced in experiments with low or zero c-C_6H_{12} concentrations. The unimolecular rate constant k_{obs} was determined by a linear fit to the first five data points. Under pseudo-first-order conditions, the observed rate constant k_{obs} is related to the bimolecular rate constant by

$$k_{obs} = k_{eff}[O_3] \tag{6}$$

For the calculation of k_{eff} the experimentally determined mean concentrations of ozone were used. When cyclohexane was added before the start of an experiment, k_{eff} decreased. The dependence of k_{eff} on the amount of c-C_6H_{12} present (at constant initial concentrations of the alkene and ozone) is shown in Figure 2.

Although the formation of the OH radical was questioned in an article by Schäfer et al.,[5] strong evidence for direct OH radical formation was obtained in recent studies using spectroscopic methods.[6,30] Indirect evidence supporting the formation of OH radicals comes from relative rate studies.[18,19,21] Therefore, the measured variation of k_{eff} was related to the OH radical yield. The analysis is based on the following reactions:

$$\text{alkene} + O_3 \rightarrow \text{products} + Y_{OH}OH \tag{7}$$

$$\text{alkene} + OH \rightarrow \text{products} \tag{8}$$

$$c\text{-}C_6H_{12} + OH \rightarrow \text{products} \tag{9}$$

where Y_{OH} corresponds to the yield of the OH radical formed in the ozonolysis reaction. At the early stages of the reaction, OH radicals will almost exclusively react with alkene or with c-C_6H_{12}, if present.

With reactions 7−9 proceeding, products formed in these reactions also react with OH radicals, thus diminishing the consumption of the alkene by reaction 8 at later stages of the reaction. Thus, the slight curvature in the ln(absorption) profiles,

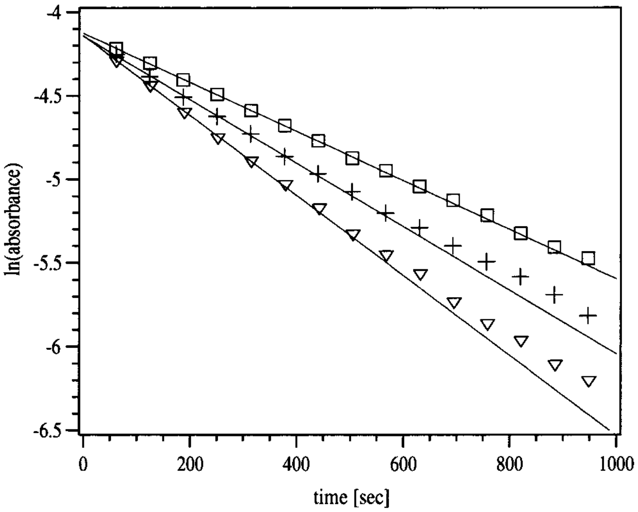


Figure 1. Profile of ln(absorption) of isobutene. Initial concentrations of ozone and isobutene are 1.2×10^{14} and 1.2×10^{13} molecule cm^{-3}, respectively. Cyclohexane concentrations used are zero (triangles), 7.0×10^{13} molecule cm^{-3} (crosses), and 9.8×10^{14} molecule cm^{-3} (squares).

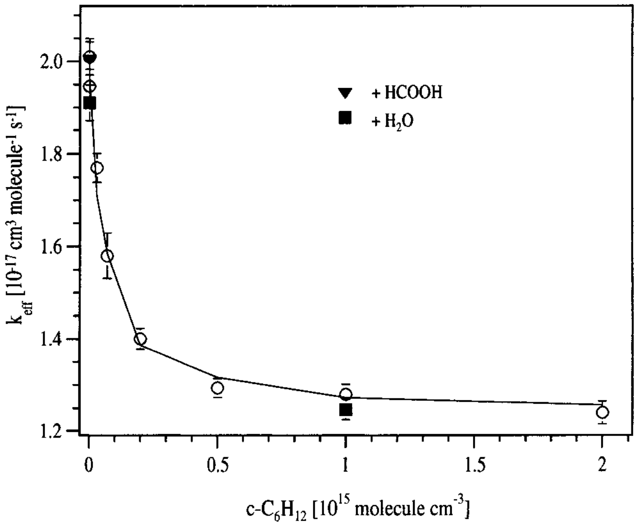


Figure 2. Dependence of k_{eff} on $[c\text{-}C_6H_{12}]_0$. Open circles represent measured rate constants. Also shown are data from experiments in the presence of HCOOH (filled triangle) and H_2O (filled squares). The solid line represents calculated values for k_{eff} using eq 13 (see text).

corresponding to a decreasing k_{eff}, can be explained by an increasing importance of the reactions of the OH radical with products of reactions 7 and 8. Products from reactions 7 and 8, which are most reactive versus oxidation by the OH radical, are presumably formaldehyde (HCHO), acetaldehyde (CH_3CHO), and methacrolein ($CH_2{=}C(CH_3)CHO$) for the different alkenes investigated in this study. Rate coefficients for the reaction of the OH radical with these carbonyl compounds are, however, a factor of 2−3 smaller than k_8 of the reaction of the OH radical with the parent alkene. At the initial stages of the reaction the OH radical will therefore predominantly react with the alkenes and reactions 7−9 should be a good representation of the chemical system.

It should be also pointed out that the OH radical yield (Y_{OH}) represents an overall yield that also includes a possible contribution from the reaction of the HO_2 radical with O_3.

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{10}$$

In the presence of oxygen, HO_2 radicals can be formed from the decomposition channels of the excited Criegee intermediate CH_2OO^*.[31] Another source of HO_2 radicals are reactions of oxygen with alkoxy radicals, which are formed in peroxy radicals reactions of the products formed in reactions 7−9. The occurrence of reaction 10 is a major contributor to the uncertainty of the OH radical yield obtained in this study. On the basis of the explicit chemical mechanism of the isobutene−O_3 system discussed below, we estimate that about 5% of the total OH radical formed arises from reaction 10. Compared to the overall yield of OH radicals in the chemical systems investigated, formation of OH radicals due to reaction 10 is of minor importance. The decrease of the alkene concentration can therefore be described by reactions 7−9:

$$-\mathrm{d[alkene]}/\mathrm{d}t = k_7[O_3][\mathrm{alkene}] + k_8[OH][\mathrm{alkene}] \tag{11}$$

The OH radical concentration can be approximated by assuming steady-state conditions:

$$[OH]_{ss} = \frac{k_7 Y_{OH}[O_3][\mathrm{alkene}]}{k_8[\mathrm{alkene}] + k_9[c\text{-}C_6H_{12}]}$$

Inserting $[OH]_{ss}$ in eq 11 yields

$$-\frac{\mathrm{d[alkene]}}{\mathrm{d}t} = k_7[O_3][\mathrm{alkene}]\left(1 + \frac{Y_{OH}}{1+\alpha}\right) \tag{12}$$

with

$$\alpha = \frac{k_9[c\text{-}C_6H_{12}]}{k_8[\mathrm{alkene}]}$$

Application of expression 12 is easy for experiments that were performed without c-C_6H_{12} addition or with c-C_6H_{12} concentration in large excess of the concentration of the alkene. In the presence of sufficient c-C_6H_{12} to scavenge virtually all OH radicals, $\alpha \gg 1$ and expression 12 reduces to

$$-\frac{\mathrm{d[alkene]}}{\mathrm{d}t}\bigg|_{\alpha\gg 1} = k_7[O_3][\mathrm{alkene}] \tag{13}$$

which means that under these conditions (excess c-C_6H_{12}) the experimentally determined k_{eff} of the pseudo-first-order decay is equal to $k_7[O_3]$. The rate constants for propene, isobutene, and isoprene are determined from experiments with $\alpha \gg 1$ (excess c-C_6H_{12} as OH scavenger) and are given in Table 1.

TABLE 1: Rate Constants for the Reaction of Ozone with Propene, Isobutene, and Isoprene

	k_{O3} [cm^3 molecule^{-1} s^{-1}]	
propene	1.15×10^{-17}	this work
	0.96×10^{-17}	43
	1.26×10^{-17}	44
isobutene	1.24×10^{-17}	this work
	1.20×10^{-17}	36
	1.15×10^{-17}	45
isoprene	1.30×10^{-17}	this work
	1.27×10^{-17}	43
	1.22×10^{-17}	45

TABLE 2: OH Radical Yields in the Gas-Phase Reaction of Ozone with Propene, Isobutene, and Isoprene

	OH radical yield	literature
propene	$0.34^{+0.03}_{-0.06}$	this work
	$0.33^{+0.16}_{-0.11}$	3
	0.35 ± 0.07	21
	0.18 ± 0.02	17
isobutene	$0.60^{+0.05}_{-0.07}$	this work
	0.84 ± 0.42	3
isoprene	$0.26^{+0.03}_{-0.06}$	this work
	0.19 ± 0.02	17
	0.65 ± 0.15[a]	6
	$0.27^{+0.13}_{-0.09}$	2
	0.25 ± 0.06	32

[a] Performed at low pressure.

Values of the rate constants derived in this study are in excellent agreement with those recommended by Atkinson.[13]

For experiments that were performed without addition of c-C_6H_{12}, α equals zero and expression 12 reduces to

$$-\frac{\mathrm{[alkene]}}{\mathrm{d}t}\bigg|_{\alpha=0} = k_7(1 + Y_{OH})[O_3][\mathrm{alkene}] = k_{eff}[O_3][\mathrm{alkene}] \tag{14}$$

By use of the value of k_7 determined in the presence of excess c-C_6H_{12}, the yield of OH radicals is directly related to k_{eff} by $Y_{OH} = (k_{eff} - k_7)/k_7$. In Table 2 our evaluated OH radical yields are shown for propene, isobutene, and isoprene and are compared to literature values. The OH yields of isoprene (26%) and propene (34%) measured in the present study fit well with yields measured by the groups of Atkinson[2,3] and Paulson[32,21] but appear to be significantly higher than those reported in the study of Gutbrod et al.[17] Some disagreement about the OH yield of isobutene (60%) exists between the study of Atkinson et al.[3] and this study. Their value of 0.84 for isobutene is also relatively high compared to the 0.70 OH yield for 2,3-dimethyl-2-butene reported by the same group.[16] Since very few OH radicals are formed from the decomposition of the CH_2OO^* Criegee intermediate, it is expected that fewer OH radicals are formed in the ozonolysis of isobutene because fewer $(CH_3)_2COO^*$ Criegee intermediates are formed.

It is generally assumed that the OH radicals, whose formation has been observed indirectly by several methods, originate from the decomposition of the excited Criegee intermediate. However, very little is known about the reactions of the stabilized Criegee intermediate. Reactions of the stabilized Criegee intermediate with H_2O have been suggested as the source of OH radicals in the reaction of isoprene and O_3[14] and were incorporated into the RADM mechanism[33] as a source of OH radicals. To investigate the possibility that reactions of the stabilized Criegee intermediate might alter the extent of OH radical formation,

TABLE 3: Product Yields and Modeled Results of the Ozonolysis of Isobutene[a]

	without CO		with CO (1.2×10^{18} molecule cm^{-3})	
	exptl	calcd ($n = 3313$)[b]	exptl	calcd ($n = 3114$)[b]
Δ(isobutene)/$\Delta(O_3)$	1.56 ± 0.10	1.50 ± 0.04	1.05 ± 0.07	0.96 ± 0.13
HCHO	1.21 ± 0.13	1.45 ± 0.16	0.97 ± 0.11	1.00 ± 0.20
$CH_3C(O)CH_3$	0.51 ± 0.06	0.43 ± 0.09	0.30 ± 0.03	0.28 ± 0.06
$CH_3C(O)CHO$	0.17 ± 0.03	0.09 ± 0.05	0.15 ± 0.03	0.05 ± 0.03
$CH_3C(O)CH_2OH$	0.09 ± 0.02	0.06 ± 0.04	0.07 ± 0.015	0.04 ± 0.03
CO	0.15 ± 0.02	0.14 ± 0.02	n.d.	n.d
CO_2	0.35 ± 0.07	0.45 ± 0.08	0.93 ± 0.2	0.88 ± 0.08
CH_3OH	0.07 ± 0.01	0.05 ± 0.03	0.04 ± 0.005	0.02 ± 0.01
HCOOH	0.08 ± 0.01	0.05 ± 0.01	0.09 ± 0.01	0.04 ± 0.01
$H_2C{=}CO$	0.005 ± 0.002	0	0.005 ± 0.002	0
$CH_3C(O)CH_2OOH$	n.d.	0.05 ± 0.04	n.d.	0.18 ± 0.09
$(CH_3)_2C(OOH)CH_2OH$[c]	n.d.	0.35 ± 0.10	n.d.	0.03 ± 0.01

[a] Initial isobutene and ozone concentrations were 4.8×10^{14} and 2.4×10^{14} molecule cm^{-3}, respectively. Experimental yields were determined relative to $\Delta(O_3)$ after completion of the reaction ($[O_3] < 4.8 \times 10^{12}$ molecule cm^{-3}). n.d. ≡ not determined. [b] Calculated yields are from a total of n simulations with varied rate constants. [c] The formation of $(CH_3)_2C(OH)CH_2O_2H$ was not considered in the chemical mechanism (see Table 4).

several experiments with added scavengers for the stabilized Criegee intermediate were performed. H_2O and HCOOH were chosen as scavengers for the stabilized Criegee intermediate formed in the ozonolysis of the investigated alkenes. On the basis of published relative rate constants for the stabilized Criegee intermediate,[34] we estimate that H_2O in a concentration of 2×10^{18} molecule cm^{-3} (corresponding to a relative humidity (RH) of 30% at 295 K) would dominate the bimolecular reactions of the stabilized Criegee intermediate under the experimental conditions used. HCOOH was also used as a scavenger for the stabilized Criegee intermediate because various recent investigations[35,26] have shown that organic acids react very rapidly with stabilized Criegee intermediates. When either 3.6×10^{13} molecule cm^{-3} HCOOH or 2×10^{18} molecule cm^{-3} H_2O was added before the alkene was introduced, no significant change in k_{eff} was found compared to experiments without reaction partners for the stabilized Criegee intermediate (Figure 2). From the FTIR spectra it was evident that reactions of the stabilized Criegee intermediate have taken place. When, for example, H_2O was added, an increase in HCOOH was observed as is expected from the proposed reaction of the stabilized Criegee intermediate CH_2OO:[36]

$$CH_2OO + H_2O \rightarrow HOCH_2OOH \qquad (15)$$

$$HOCH_2OOH \rightarrow HCOOH + H_2O \qquad (16)$$

We therefore conclude that no bimolecular reaction is producing OH radicals in the ozonolysis of the alkenes investigated except for some minor contribution of reaction 10 as discussed above. These results are in line with the results from Atkinson et al.,[2] who found that the OH radical yield in the α-pinene–ozone reaction is independent of $[H_2O]$.

So far, only the two extreme cases of experiments with either no c-C_6H_{12} addition or the presence of c-C_6H_{12} in large excess concentrations have been analyzed. To relate α with the measured k_{eff} value in a direct way, α was assumed to be constant with time. While this is a good approximation for $[c\text{-}C_6H_{12}]$, the alkene concentration has decreased typically by 35–55% when data acquisition stopped. The solid line in Figure 2 shows the calculated k_{eff}, determined using the average measured alkene concentration, the rate constant k_7, and the OH radical Y_{OH} yield as described in eq 12. Since the decrease of k_{eff} is sensitive to the rate constants k_8 and k_9, the excellent agreement of the calculated values with the measured values provides further evidence for the formation of OH radicals.

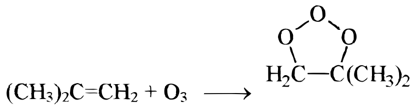
From a number of recent studies, in particular from those reporting the direct observation of OH radicals,[6,30] it is clear beyond reasonable doubt that OH radicals are formed as products of the alkene–ozone reaction. In view of this evidence the question raised by Schäfer et al.[5] "Is the hydroxyl radical really formed in the gas-phase ozonolysis of alkenes?" should be answered with yes. The discrepancies in the relative consumption of pairs of tracers reported in Schäfer et al.[5] originate most likely from an underestimation of the experimental uncertainties. Schäfer et al.[5] assumed an error of 0.3% for their GC analysis, which is unrealistically low. A better estimation of typical errors using the GC method is given by Paulson et al.[18]

Product Yields. Ozonolysis experiments were performed at concentrations of 4.8×10^{14} molecule cm^{-3} isobutene and 2.4×10^{14} molecule cm^{-3} of ozone. Under these experimental conditions, more than 90% of the ozone reacts within 10 min, so no attempt to achieve time-resolved product concentrations was made. CO was chosen as an OH radical scavenger, since the oxidation of CO is well-known and does not add to the complexity of the chemical system.

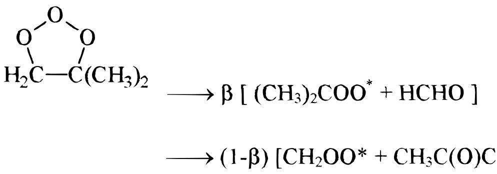
$$OH + CO \rightarrow CO_2 + H \qquad (17)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (18)$$

Product yields of the ozonolysis of isobutene are given in Table 3. In the presence of CO, the only source of acetone is the decomposition of the primary isobutene ozonide, therefore allowing the determination of the branching ratio of the primary isobutene ozonide:



(19)



(20a)

(20b)

The acetone yield of 30% (Table 3) implies the formation of the $(CH_3)_2COO^*$ and CH_2OO^* intermediates at 70% and 30% yields, respectively, corresponding to a value of $\beta = 0.70$. Decomposition pathways for the CH_2OO^* intermediate are taken from a recent investigation of the ozonolysis of ethene.[27] It should be noted that the relative importance of the various reaction pathways of Criegee intermediates of identical structure, but originating from different alkenes, is not necessarily identical.

The total OH radical yield in the isobutene−ozone system in this work (see Table 2) has been determined to be 60%. On the basis of the 12% OH radical yield for the ethene−ozone reaction (which also includes some contribution of reaction 10)[2] and preliminary runs of the numerical model described in Table 4, we estimate the contribution of OH radical production from the decomposition of the CH_2OO^* intermediate and reaction 10 to be approximately 5%, making the hydroperoxide channel (reaction 22) the major decomposition reaction for the $(CH_3)_2COO^*$ intermediate, accounting for 55% of the total OH radical production (all percentages are relative to conversion of isobutene via reaction 19). It should be pointed out that a possible underestimation of the OH radical production due to reaction 10 or the decomposition of the CH_2OO^* intermediate is counteracted by the inherent underestimation of OH radical yields in our scavenger experiments caused by the only 95% OH radical scavenging efficiency.

The extent of stabilization (reaction 23) was estimated by using data from Hatakeyama et al.[37] who determined an 18% yield for $((CH_3)_2COO + CH_2OO)$. Again, assuming the same extent of stabilization for the CH_2OO^* intermediate formed in the ozonolysis of ethene and isobutene, we estimate a 50% stabilization for the CH_2OO^* intermediate based on the data of Neeb et al.[27] and Hatakeyama et al.[37] The latter authors are usually cited with an extent of 39% stabilization,[13] which however must be corrected with the 7% increase in HCOOH originating from a bimolecular reaction of the CH_2OO intermediate.[38] Since 30% of the CH_2OO^* intermediate is formed, most of the yield determined by Hatakeyama et al.[37] is due to reactions of the CH_2OO intermediate and only about 3% is due to the formation of the $(CH_3)_2COO$ intermediate. Having evaluated two out of three channels (reactions 21−23) discussed, the extent of the CO_2 eliminating channel is estimated to be 12%. In the ozonolysis of *trans*- and *cis*-2-butene the formation of methane was observed[22] and propene has been found as a product of isoprene.[14] The formation of these hydrocarbons has been explained from a shift of an H atom simultaneously with CO_2 formation from the Criegee intermediate (reaction 3b). In the ozonolysis of isobutene the formation of ethane could not be observed (upper limit of 2%) presumably because of the higher stability of the leaving radicals (CH_3 vs H). The reactions pathways of the excited $(CH_3)_2COO^*$ intermediate under atmospheric pressure are therefore described by reactions 21−23. Normalized to unity, the branching ratios of reactions 21, 22, and 23 are 0.17, 0.78, and 0.05, respectively.

$$(CH_3)_2COO^* \rightarrow CO_2 + 2CH_3 \tag{21}$$

$$(CH_3)_2COO^* \rightarrow CH_3C(OOH){=}CH_2^* \rightarrow CH_3C(O){=}CH_2 + OH \tag{22}$$

$$(CH_3)_2COO^* + M \rightarrow (CH_3)_2COO + M \tag{23}$$

The extent of stabilization of the $(CH_3)_2COO^*$ intermediate originating from the ozonolysis of isobutene is significantly lower than the 30% stabilization determined by Niki et al.[1] for the 2,3-dimethyl-2-butene−ozone reaction. In their study Niki et al.[1] determined the extent of OH radical production via reaction 22 but did not consider the ester channel (reaction 21). It remains unclear if this is the reason for the apparent discrepancy of the fact that the Criegee intermediate originating from different alkenes does not necessarily behave identically.

On the basis of the branching ratios for Criegee intermediates $(CH_3)_2COO^*$ and CH_2OO^*, a detailed numerical simulation was set up. Reactions of the stabilized Criegee intermediate CH_2OO were taken from Neeb et al.[27] The small fraction of stabilized $(CH_3)_2COO$ intermediate present was assumed to react similarly to the CH_2OO intermediate except that secondary isobutene ozonide is formed in its reaction with HCHO (Table 4).

All reactions to simulate the isobutene ozonolysis are shown in Table 4. To describe the chemical system, it was necessary to include the chemistry of several peroxy radicals that are formed under the experimental conditions employed in this study. OH radicals that are formed in reaction 22 react in the absence of a scavenger with the alkene, causing the observed excess alkene consumption and formation of α-hydroxy peroxy radicals. The decomposition of the Criegee intermediate according to reactions 21−23 provides another source of peroxy radicals that is also present in the presence of CO as OH radical scavenger.

The reactions of the $CH_3C(O)CH_2O_2$ radical, which is formed in the reaction of OH radicals with acetone, were found to have a major influence on the calculated product yields.

$$CH_3C(O)CH_3 + OH\ (+O_2) \rightarrow CH_3C(O)CH_2O_2 + H_2O \tag{24}$$

In the isobutene−ozone system the $CH_3C(O)CH_2$ radical is expected to originate from the decomposition of the Criegee intermediate via the hydroperoxide channel (reaction 22) after isomerization of the alkenoxy radical $CH_3C(O){=}CH_2$:

$$[CH_3C(O){=}CH_2 \leftrightarrow CH_3C(O)CH_2] + O_2 + M \rightarrow CH_3C(O)CH_2O_2 + M \tag{25}$$

Rate constants for the peroxy radical reactions were taken from the most recent IUPAC recommendations.[25] Rate constants for the $(CH_3)_2C(O_2)CH_2OH$ radical, which is the most probable peroxy radical formed in the reaction of isobutene with OH radicals (Markovnikoff's rule), are not known and were estimated using the geometric mean rule.[13] Branching ratios for the reactions of the $(CH_3)_2C(O_2)CH_2OH$ radical and the rate constant for its self-reaction were taken from the recommendations of Jenkin et al.[39] To reduce the complexity of the chemical mechanism, the formation of the $(CH_3)_2C(OH)CH_2O_2$ radical was not considered, though rate constants for this peroxy radical are available from studies of the oxidation of *tert*-butyl alcohol.[40] The oxidation of HCHO, initiated by its reactions with the HO_2 radical,[41] was not incorporated either. The calculated product yields from the simulation runs were not significantly affected (less than 0.2%) when the corresponding reactions were added.

Calculated yields are compared to experimental values in Table 3. For the calculated yields of a product the entire set of calculated product yields could be analyzed using the Gaussian distribution. In Figure 3 the distribution of HCHO yields is shown and compared to a fitted distribution. The high variability of the calculated HCHO yield is not unexpected, since part of the HCHO is formed from the reactions of the CH_3O_2 and $CH_3C(O)CH_2O_2$ radicals and therefore is subject to numerous uncertainties. Errors for the calculated yields in Table 3 correspond to $\pm 2\sigma$ and reflect the overall uncertainties associated with the reactions leading to the observed products.

TABLE 4: Explicit Chemical Mechanism for the Isobutene−Ozone System[a]

no.	reaction	rate constant[b]	error, $E = \log(\Delta k)$
19	$(CH_3)_2C{=}CH_2 + O_3 \rightarrow POZ$	1.2×10^{-17}	0.08
	$(CH_3)_2C{=}CH_2 + OH\ (+O_2) \rightarrow RO_2$	5.1×10^{-11}	0.08
20a	$POZ \rightarrow (CH_3)_2COO^* + HCHO$	$1 \times 10^{8}(1 - \alpha_1)$	
20b	$POZ \rightarrow CH_2OO^* + CH_3COCH_3$	$1 \times 10^{-8}\alpha_1$	
	$CH_2OO^* \rightarrow CO_2 + 2\ H$	0.10×10^{6}	
	$CH_2OO^* \rightarrow CO_2 + H_2$	0.13×10^{6}	
	$CH_2OO^* \rightarrow CO + H_2O$	0.13×10^{6}	
	$CH_2OO^* \rightarrow HCO + OH$	0.10×10^{6}	
	$CH_2OO^* \rightarrow HCOOH$	0.04×10^{6}	
	$CH_2OO^* + M \rightarrow CH_2OO + M$	$0.50 \times 10^{6}/M$	
23	$(CH_3)_2COO^* + M \rightarrow (CH_3)_2COO + M$	$0.05 \times 10^{6}/M$	
22	$(CH_3)_2COO^* \rightarrow CH_3COCH_2 + OH$	0.78×10^{6}	
21	$(CH_3)_2COO^* \rightarrow 2CH_3 + CO_2$	0.17×10^{6}	
	$CH_2OO + HCHO \rightarrow HCOOH + HCHO$	$k_C(4 \times 10^{-14})$[c]	
	$CH_2OO + HCOOH \rightarrow HPMF$	$k_C(60 \times 10^{-14})$	
	$(CH_3)_2COO + HCHO \rightarrow SOZ$	$k_C(4 \times 10^{-14})$	
	$(CH_3)_2COO + HCOOH \rightarrow (CH_3)_2C(O_2H){-}O{-}CHO$	$k_C(60 \times 10^{-14)}$	
	HO_x Chemistry		
18	$H + O_2\ (+M) \rightarrow HO_2$	7.5×10^{-11}	
	$CH_3 + O_2\ (+M) \rightarrow CH_3O_2$	1.8×10^{-12}	
10	$O_3 + HO_2 \rightarrow OH + 2O_2$	2×10^{-15}	0.2
	$2HO_2 \rightarrow H_2O_2 + O_2$	2.8×10^{-12}	0.15
	$HCHO + OH \rightarrow HCO + H_2O$	9.2×10^{-12}	0.1
	$HCO + O_2 \rightarrow CO + HO_2$	5.5×10^{-12}	
	$CO + O_3 \rightarrow CO_2 + O_2$	1×10^{-22}	1.0
17	$CO + OH \rightarrow HO_2 + CO_2$	2.0×10^{-13}	0.2
	Peroxy−Peroxy Radical Reactions		
25	$CH_3COCH_2 + O_2 \rightarrow CH_3COCH_2O_2$	1.5×10^{-12}	
	$2CH_3COCH_2O_2 \rightarrow 2CH_3COCH_2O + O_2$	6.0×10^{-12}	0.3
	$2CH_3COCH_2O_2 \rightarrow HYACE + MGLY + O_2$	2.0×10^{-12}	0.5
	$2CH_3COO_2 \rightarrow 2CH_3COO + O_2$	1.6×10^{-11}	0.5
	$2RO_2 \rightarrow 2RO + O_2$	1.7×10^{-14} [d]	1.0
	$2CH_3O_2 \rightarrow 2CH_3O + O_2$	$3.7 \times 10^{-13}\alpha_2$	0.12
	$2CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$	$3.7 \times 10^{-13}(1 - \alpha_2)$	0.12
	Peroxy−HO_2 Radical Reactions		
	$RO_2 + HO_2 \rightarrow ROOH + O_2$	1.5×10^{-11}	0.5
	$CH_3COCH_2O_2 + HO_2 \rightarrow CH_3COCH_2O_2H + O_2$	9.0×10^{-12}	0.3
	$CH_3COO_2 + HO_2 \rightarrow CH_3COO_2H + O_2$	1.0×10^{-11}	0.3
	$CH_3COO_2 + HO_2 \rightarrow CH_3COOH + O_3$	3.6×10^{-12}	0.3
	$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$	5.2×10^{-12}	0.3
	Peroxy−Peroxy Cross Reactions		
	$CH_3COCH_2O_2 + RO_2 \rightarrow CH_3COCH_2O + RO + O_2$	$7.4 \times 10^{-13}\alpha_3$[d]	1.0
	$CH_3COCH_2O_2 + RO_2 \rightarrow CH_3COCHO + P1 + O_2$	$7.4 \times 10^{-13}(1 - \alpha_3)$[d]	1.0
	$CH_3COO_2 + RO_2 \rightarrow CH_3COO + RO + O_2$	1.0×10^{-12} [d]	1.0
	$RO_2 + CH_3O_2 \rightarrow RO + CH_3O + O_2$	$1.6 \times 10^{-13}\alpha_4$[d]	1.0
	$RO_2 + CH_3O_2 \rightarrow P1 + HCHO + O_2$	$1.6 \times 10^{-13}(1 - \alpha_4)$[d]	1.0
	$CH_3COCH_2O_2 + CH_3COO_2 \rightarrow CH_3COCHO + CH_3COOH + O_2$	$5.0 \times 10^{-12}(1 - \alpha_5)$	0.5
	$CH_3COCH_2O_2 + CH_3COO_2 \rightarrow CH_3COCH_2O + CH_3COO + O_2$	$5.0 \times 10^{-12}\alpha_5$	0.5
	$CH_3COCH_2O_2 + CH_3O_2 \rightarrow CH_3COCH_2O + CH_3O + O_2$	$3.8 \times 10^{-12}\alpha_6$	0.3
	$CH_3COCH_2O_2 + CH_3O_2 \rightarrow CH_3OH + O_2$	$3.8 \times 10^{-12}(1 - \alpha_6)/2$	0.3
	$CH_3COCH_2O_2 + CH_3O_2 \rightarrow CH_3COCH_2OH + HCHO + O_2$	$3.8 \times 10^{-12}(1 - \alpha_6)/2$	0.3
	$CH_3COO_2 + CH_3O_2 \rightarrow CH_3COO + CH_3O + O_2$	1.1×10^{-11}	0.3
	$CH_3COO_2 + CH_3O_2 \rightarrow CH_3COOH + HCHO + O_2$	1.8×10^{-12}	0.5
	Decomposition of Alkoxyradicals		
26	$CH_3COCH_2O\ (+O_2) \rightarrow HCHO + CH_3COO_2$	1×10^{6}	
	$CH_3COO\ (+O_2) \rightarrow CH_3O_2 + CO_2$	1×10^{6}	
	$CH_3O + O_2 \rightarrow HCHO + HO_2$	1.9×10^{-15}	
	$RO \rightarrow CH_3COCH_3 + HCHO + HO_2$	1×10^{6}	

[a] Unless otherwise stated, rate constant are taken from Atkinson et al.[25] Values for the branching ratios α1−α6 were taken from Jenkin et al.:[39] $\alpha 1 = 0.3 \pm 0.05$; $\alpha 2 = 0.3 \pm 0.1$; $\alpha 3 = 0.7 \pm 0.2$; $\alpha 4 = 0.7 \pm 0.2$; $\alpha 5 = 0.7 \pm 0.2$; $\alpha 6 = 0.6 \pm 0.2$. SOZ = secondary isobutene ozonide; POZ = primary isobutene ozonide; RO_2 equals $(CH_3)_2C(O_2)CH_2OH$; RO is the corresponding alkoxy radical $(CH_3)_2C(O)CH_2OH$; P1 = $(CH_3)_2C(OH)CH_2OH$. [b] Rate constants for bimolecular and unimolecular reactions are given in cm^3 $molecule^{-1}$ s^{-1} and s^{-1}, respectively. [c] Absolute rate constants for reactions of the stabilized Criegee intermediate are not available. The value of k_C has arbitrarily been set to 1. [d] Rate constants were derived by the geometric mean rule $k_{12} = 2(k_1k_2)^{1/2}$ with k_1 and k_2 being the rate constants for the self-reactions of the peroxy radicals participating in the reaction.

Both in the absence and presence of CO, the calculated product yields are in good agreement with experimental data. In Table 3 experimental product yields are compared to calculated yields using the chemical scheme described in Table 4. The agreement is excellent for the alkene consumption, HCHO and acetone, CO and CO_2. The only compounds whose experimental yields are clearly different from the modeled results are HCOOH and methylglyoxal. HCOOH concentrations are

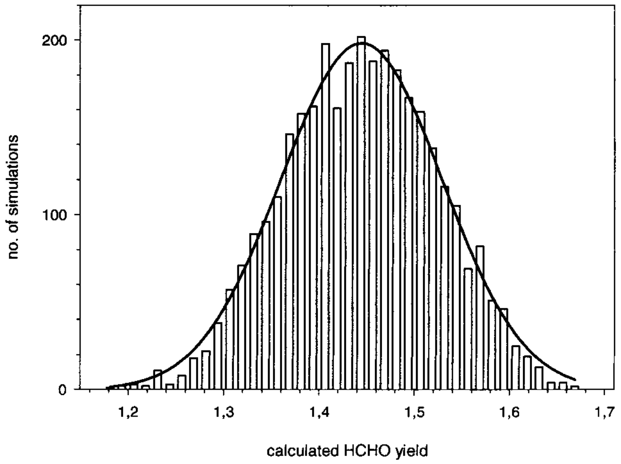


Figure 3. Calculated HCHO yields (Δ(HCHO)/Δ(ozone)) in the isobutene−ozone system in the presence of excess CO. Rate constants used in the simulation (Table 4) were varied according to a normal distribution (see text). The total number of simulations was 3313. The width of a histogram bars is 0.0125.

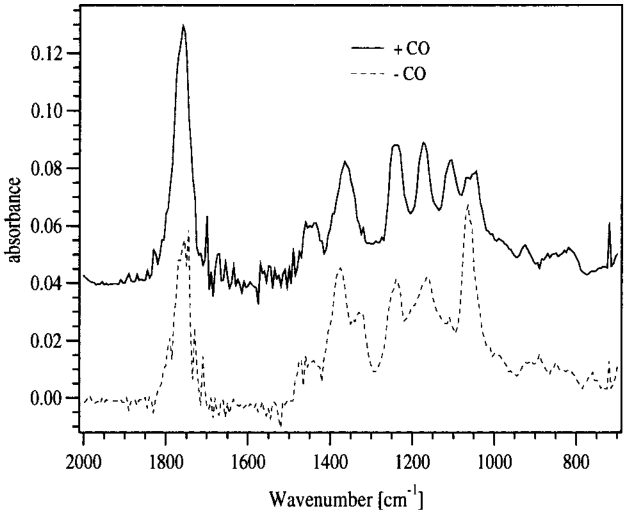


Figure 4. FTIR spectra (700−2000 cm^{-1}) after computational subtraction of the absorbance of products listed in Table 3: (solid line) in the presence of CO; (dashed line) without CO addition.

largely controlled by the reactions of the stabilized CH_2OO intermediate (see Table 4), which introduce considerable uncertainty. The reactions of the CH_2OO intermediate with HCHO and HCOOH, which are of some relevance in our laboratory study, are unimportant under tropospheric conditions. Therefore, no attempt was made to find a better set of rate constants for the reactions of the stabilized Criegee intermediates. The experimentally obtained yield for methylglyoxal is larger than the calculated yield by a factor of 3. Even taking into account the fairly large error in calculated yields, the model results are clearly too low. It cannot be ruled out that our experimentally determined methylglyoxal yield is too high because absorptions of unidentified products can add to the absorption used for the quantification of methylglyoxal. In a previous investigation of the isobutene ozonolysis, Grosjean et al.[42] found a yield of 19% for the sum of methylglyoxal and hydroxyacetone, which is comparable to the results of this study. Since the experimental yield of hydroxyacetone is also higher than those calculated, it appears possible that an underestimation of the rate constant for the self-reaction of the $CH_3C(O)CH_2O_2$ radical might lead to the observed discrepancy. Another possibility is that the $CH_3C(O)CH_2O$ alkoxy radical does not decompose exclusively but also reacts with molecular oxygen:

$$CH_3C(O)CH_2O \rightarrow CH_3CO + HCHO \qquad (26a)$$

$$CH_3C(O)CH_2O + O_2 \rightarrow CH_3C(O)CHO + HO_2 \qquad (26b)$$

So far, there is no evidence for the occurrence of reaction 26b,[24] and so the numerical scheme was left to conform to IUPAC recommendations.[25]

Two major products ($CH_3C(O)CH_2OOH$ and $(CH_3)_2C(OOH)CH_2OH$) were not measured by FTIR spectroscopy because of the absence of reference compounds. In the absence of CO it is likely that most of the $(CH_3)_2C(O_2)CH_2OH$ radical reacts with HO_2 radicals, forming the corresponding hydroperoxide (Table 3). In the presence of CO, the concentration of the HO_2 radical can be expected to be enhanced because of reactions 17 and 18. Under these conditions the organic hydroperoxide-forming reaction of the $CH_3C(O)CH_2O_2$ radical with HO_2 radicals will be more important than the self-reaction of the $CH_3C(O)CH_2O_2$ radical, leading to lower yields of methylglyoxal and hydroxyacetone, as is observed experimentally. In Figure 4, a comparison of the spectra in the absence and presence of CO is shown after computational subtraction of the absorbance of the products listed in Table 3. According to the results of the chemical modeling, the major contributors to these spectra should be the hydroperoxides $CH_3C(O)CH_2OOH$ and $(CH_3)_2C(OOH)CH_2OH$. The modeled yield of $(CH_3)_2C(OOH)CH_2OH$ also represents the yield of $(CH_3)_2C(OH)CH_2OOH$ hydroperoxide, since only one β-hydroxy peroxy radical is allowed to form in the chemical scheme. Minor amounts of diols and hydroxycarbonyl compounds containing four carbon atoms may also contribute to the spectra shown in Figure 4.

Conclusions

The rate constants for the reaction of ozone with propene, isobutene, and isoprene, which were determined in the presence of cyclohexane, are in excellent agreement with recommended values. The OH radical yields for propene, isobutene, and isoprene have been redetermined on the basis of a novel method monitoring the pseudo-first-order decay rate of the alkene under excess ozone conditions. From the results of the experiments in the presence of H_2O and HCOOH, it appears that reactions of the stabilized Criegee intermediate have no effect on OH radical production. In contrast to the previous publication by Schäfer et al.,[5] no evidence for the Criegee intermediate acting as oxidant was found. The value for the OH radical yield of isobutene (60%) was used for the development of an explicit chemical mechanism of the isobutene ozonolysis in the gas phase. Comparison of calculated product yields with experimental values from this study shows that most experimentally found products can be quantitatively explained by the simple Criegee mechanism and the secondary chemistry of the peroxy radicals used in the simulation.

The discussed three pathways (reaction 3−5) for the Criegee intermediate imply an inverse relationship between OH yield and the degree of stabilization. This assumption should hold true as long as the CO_2 eliminating channel (reaction 3) either is of minor importance or contributes to a rather constant percentage to the decomposition channels of different Criegee intermediates. While OH radical yields are available for a number of alkenes and dialkenes, much less data are available about the degree of stabilization. The single most extensive data set comes from Hatakeyama et al.[37] who used the oxidation of SO_2 to SO_3 by reaction with the Criegee intermediate as a

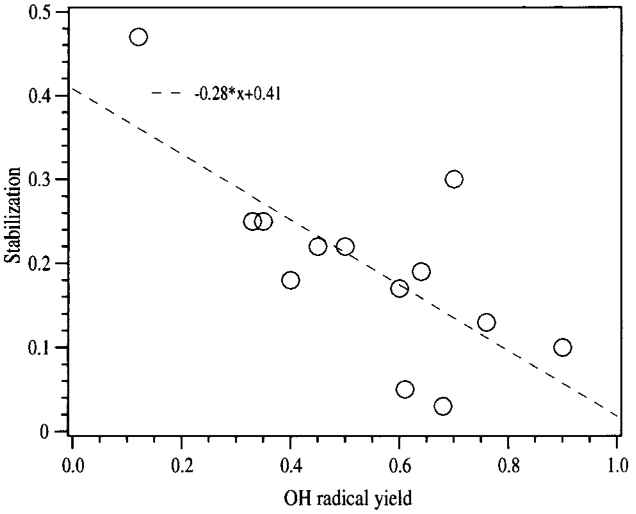


Figure 5. Relation between the yields of OH radicals and stabilized Criegee intermediates. The line represents an unweighted linear regression. Alkenes in the order of increasing OH radical yield are ethene, propene, β-pinene, *cis*-2-butene, 1-octene, methylene-cyclohexene, isobutene, cyclopentene, *trans*-2-butene, cyclohexene, 2,3 dimethyl-2-butene, α-pinene, and 1-methylcyclohexene. All data are taken from the recent review by Atkinson.[13]

quantitative measure for the extent of stabilization. The inverse correlation of the degree of stabilization and extent of OH radical formation is shown in Figure 5.

Our result suggests that most of the products of the isobutene−ozone reaction can be attributed to secondary reactions of the $CH_3C(O)CH_2O_2$ peroxy radical. Tropospheric lifetimes of alkenes range from minutes to hours, so anthropogenic alkenes emitted in urban areas are likely to react near their source. Under these conditions reactions of the formed peroxy radicals with NO dominate, and therefore, product yields will differ dramatically from NO-free conditions. According to the chemical scheme used in this study, the reaction of isobutene and O_3 in the presence of NO will yield only CO, CO_2, HCHO, HCOOH, and $CH_3C(O)CH_3$ as stable (carbon-) containing products. Formation of these products is accompanied by high peroxy radical formation originating from the decay of the $CH_3C(O)CH_2O_2$ radical. In the presence of sufficient NO and oxygen the $CH_3C(O)CH_2O_2$ radical will decompose to HCHO and CO_2 on a pathway leading to the transient formation of acetylperoxy radicals and methylperoxy radicals.

$$CH_3C(O)CH_2O_2 + 3NO + 3O_2 \rightarrow 2HCHO + CO_2 + 3NO_2 + HO_2 \quad (27)$$

The results of this study suggest that the product distributions for alkene−ozone reactions are dependent on experimental conditions. With OH yields reaching from 0.12 to 1.00,[13] it is clear that stable products largely arise from the peroxy radical ultimately formed in the hydroperoxide channel. Product yields therefore are expected to be strongly influenced by the ratio HO_2/RO_2, which itself is influenced by, for example, the initial concentrations of the OH radical scavenger of the reactants used. At least for anthropogenic alkenes the absence of NO during ozonolysis studies will probably lead to unrealistic product distributions and also underestimate HO_x production.

For the atmospherically relevant reactions of the Criegee intermediates formed in the ozonolysis of monoterpenes and sesquiterpenes, a quantitative description of the decomposition channels is not possible. By use of the hydroperoxide channel as a source of OH radicals, it appears that at least a major part of the secondary chemistry can be reduced to “normal” peroxy radical chemistry, making it easier to incorporate into tropospheric chemistry models.

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